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Infrared Investigations of Pristine Polypyrrole - Is the Polymer
Called Polypyrrole Really Poly(Pyrrole-Co-Hydroxypyrrole)?

by

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<p>Polypyrrole (Ppy) is one of the most extensively investigated of the electronically conductive polymers. Nevertheless, there is still much we don't understand about this interesting and useful material. One of the most persistent mysteries involves <u>simple chemical composition</u>. Doped PPy should have the empirical formula $C_4H_3NX_z$ where X^- is the dopant counterion and z is the fractional doping level; z is typically on the order of 0.3. However, elemental analyses of PPy typically show empirical formulas like $C_4H_3NX_zO_y$ where y ranges from 0.3 to 0.7 unaccounted for oxygen atoms per pyrrole ring. This paper presents IR spectral data which suggests that the oxygen in PPy is present as covalently-bound hydroxide. Analogous IR investigations of poly(N-methylpyrrole) films show that this polymer is also hydroxylated. The hydroxy substitution present in these polymers undoubtedly results from nucleophilic attack by water on the nascent polycationic chains.</p>					
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**INFRARED INVESTIGATIONS OF PRISTINE POLYPYRROLE - IS THE POLYMER
CALLED POLYPYRROLE REALLY POLY(PYRROLE-CO-HYDROXYPYRROLE)?**

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ABSTRACT

Polypyrrole (PPy) is one of the most extensively investigated of the electronically conductive polymers. Nevertheless, there is still much we don't understand about this interesting and useful material. One of the most persistent mysteries involves *simple chemical composition*. Doped PPy should have the empirical formula $C_4H_3NX_z$, where X^- is the dopant counterion and z is the fractional doping level; z is typically on the order of 0.3. However, elemental analyses of PPy typically show empirical formulas like $C_4H_3NX_2O_y$ where y ranges from 0.3 to 0.7 unaccounted for oxygen atoms per pyrrole ring. This paper presents IR spectral data which suggest that the oxygen in PPy is present as covalently-bound hydroxide. Analogous IR investigations of poly(N-methylpyrrole) films show that this polymer is also hydroxylated. The hydroxy substitution present in these polymers undoubtedly results from nucleophilic attack by water on the nascent polycationic chains.

Polypyrrole is one of the most extensively investigated of the electronically conductive polymers (1-10). Nevertheless, there is still much we don't understand about this polymer. One of the most persistent mysteries involves *simple chemical composition*. Doped polypyrrole should have the empirical formula $C_4H_3NX_z$, where X^- is the dopant counterion and z is the fractional doping level. However, elemental analyses of polypyrrole typically show empirical formulas like $C_4H_3NX_zO_y$, where y ranges from 0.3 to 0.7 unaccounted for oxygen atoms per pyrrole ring (2-5). While a number of explanations have been proposed (2-6), the chemical identity of this oxygen in polypyrrole is currently unknown.

Diaz et al. have, however, provided an interesting clue - this unaccounted for oxygen can be eliminated by electrochemically synthesizing the polymer in rigorously-dried acetonitrile (7,8). We have recently conducted infrared (IR) analyses on polypyrrole film synthesized in rigorously dried acetonitrile and in CH_3CN containing various amounts of water. These analyses suggest that the oxygen in polypyrrole is present as covalently-bound hydroxide. The results of these investigations are reported here.

The key to ascertaining the chemical identity of the O in polypyrrole was in obtaining reliable IR spectra for the undoped material. As recently pointed out by Zerbi, this has proved to be problematic because undoped polypyrrole is not air-stable (9,10). We have circumvented this problem by designing a novel spectroelectrochemical cell which allows for synthesis and IR and electrochemical characterization of thin polypyrrole films, while rigorously protecting these films from air (11). Polypyrrole films were synthesized galvanostatically onto an IR-transparent window in the cell (11). Polymerization solutions were 0.1 M in pyrrole and 0.1 M in $LiClO_4$. The solvent was either rigorously dried (11)

acetonitrile, as-received HPLC grade CH_3CN (this solvent contains trace, ca. 0.02 %, water), or HPLC grade CH_3CN to which was added 1 or 2 % water by volume.

The polypyrrole films synthesized from these various solvents are denoted as PPy_{dry} , $\text{PPy}_{0.02}$, $\text{PPy}_{1.0}$, and $\text{PPy}_{2.0}$. All films were ca. 400 nm thick (12). After synthesis, the polymerization solution was drained from the cell and the film was rinsed (in situ) with copious quantities of rigorously-dried CH_3CN . Excess solvent was then removed from the film by training a stream of purified (11) Ar onto the film. After drying, an IR spectrum for the doped material was obtained. The cell was then refilled with electrolyte and the film was electrochemically undoped at -0.8 V vs. SCE. The film was then rinsed and dried as before and an IR spectrum for the undoped material was obtained.

FTIR spectra for the *doped* forms of PPy_{dry} , $\text{PPy}_{0.02}$, $\text{PPy}_{1.0}$, and $\text{PPy}_{2.0}$ were, within experimental error, identical. These spectra (e.g. Figure 1) show the featureless rise in absorbance with energy, at energies above 1600 cm^{-1} , and a characteristic (9-11) series of seven absorption peaks at energies below 1600 cm^{-1} . FTIR spectra for the *undoped* films (Figure 2) are quite different. Note, for example, the dramatic attenuation in absorbance at energies above 1600 cm^{-1} ; this is expected because the absorbance in this region arises from the free charge carriers present in the doped material (5,9,13). The decreased absorbance of the undoped material allows some interesting spectral features to emerge. For example, spectra for the undoped films clearly show the N-H stretching mode at 3400 cm^{-1} .

More importantly, the spectra for the undoped films synthesized in CH_3CN containing water show a sharp peak at 3558 cm^{-1} that is not observed in PPy_{dry} (Figure 2). This peak is clearly due to an O-H stretching mode and its narrowness and position indicate that it does

not arise from water. That this O-H peak is not from water is also supported by the lack of a water bending peak at ca. 1620 cm^{-1} (14). If the 3558 cm^{-1} peak arises from covalently-bound -OH, we would expect to see a band in the region of 1260 to 1000 cm^{-1} associated with the corresponding C-O vibration (15). In agreement with this prediction, $\text{PPy}_{0.02}$, $\text{PPy}_{1.0}$, and $\text{PPy}_{2.0}$ all show an intense band at 1115 cm^{-1} ; this band is not observed in PPy_{dry} .

The identity of the 3558 cm^{-1} band can also be ascertained via an isotope exchange experiment. A polypyrrole film was synthesized in CH_3CN solution containing 1 % H_2O and then reduced as before. The film was then exposed to D_2O by filling the cell with pure liquid D_2O . The film was then dried for six hours as described above. If the 3558 cm^{-1} peak is due to O-H, exposure to D_2O should cause this band to disappear; furthermore, a new band, associated with the corresponding O-D vibration, should appear at ca. 2640 cm^{-1} (14). Figure 3 shows the infrared spectrum for the D_2O -exposed film. In agreement with the above predictions, this film shows no trace of either the 3558 cm^{-1} (O-H) or 3400 cm^{-1} (N-H) bands and two new bands at 2643 cm^{-1} (O-D) and 2571 cm^{-1} (N-D) appear (Figure 3). This isotope exchange experiment strongly supports the proposition that covalently-bound -OH is present in these polypyrrole films.

A final point is worth making about the spectrum shown in Figure 3. Note that the increase in absorbance above 1600 cm^{-1} indicates that exposure of the undoped polypyrrole film to D_2O causes the film to become partially doped. We have observed an analogous effect upon exposure of undoped polypyrrole films to H_2O . The nature of this water-induced doping process is currently unclear. We are investigating this phenomenon further.

The data obtained here indicate that the excess oxygen observed in most polypyrrole

samples is present as covalently-bound hydroxide. The investigations of Tsai et al. (16) provide an explanation for the genesis of this hydroxy substitution. As part of their investigations of substituted polythiophenes, Tsai et al. have suggested that water can undergo nucleophilic attack on the polycationic chain to yield the corresponding hydroxylated polymer (16). As in the studies described here, the water was present as a trace impurity in the acetonitrile used as the solvent for electrosynthesis (16). It seems likely that the same reaction is responsible for the hydroxy-substitution in polypyrrole.

If this is the case, other heterocyclic polymers should also be susceptible to this nucleophilic attack by water. To test this premise, we conducted analogous studies on poly(N-methylpyrrole) films. Figure 4 shows an FTIR spectrum for a poly(N-methylpyrrole) film synthesized in acetonitrile that contained 0.02 % water. The bands due to -OH are, indeed, observed and, again, these bands are not observed in films synthesized in rigorously-dried CH₃CN. Thus, nucleophilic attack by water appears to be a general phenomenon in heterocyclic polymer.

Finally, it is interesting that these polymers exist in the enol form rather than tautomerizing to the ketone. (The lack of tautomerization is supported by the absence of a carbonyl absorption in the infrared spectrum at 1710 cm⁻¹; we have shown that polypyrrole samples that are chemically-synthesized at very low rates in water show this carbonyl band (5)). That the polymer prefers to stay as the enol is, however, not too surprising because formation of the ketone would interrupt the conjugation along the polymer chain.

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FIGURE CAPTIONS

Figure 1. IR spectrum for doped polypyrrole film. This spectra is from $\text{PPy}_{1.0}$.

Figure 2. IR spectra for undoped polypyrrole films. (A) PPy_{dry} , (B) $\text{PPy}_{0.02}$, (C) $\text{PPy}_{1.0}$, (D) $\text{PPy}_{2.0}$. These spectra were arbitrarily positioned one above the other.

Hence, the ordinate is an arbitrary absorbance axis. However, as a calibration point, for each spectrum, the absorbance at $4,000\text{ cm}^{-1}$ was (A) 0.32 AU, (B) 0.95 AU, (C) 1.1 AU. (D) 1.1 AU.

Figure 3. IR spectrum for undoped $\text{PPy}_{1.0}$ after exposure of the film to D_2O .

Figure 4. IR spectrum for an undoped poly(N-methylpyrrole) film that had been synthesized in acetonitrile containing ca. 0.02% water.

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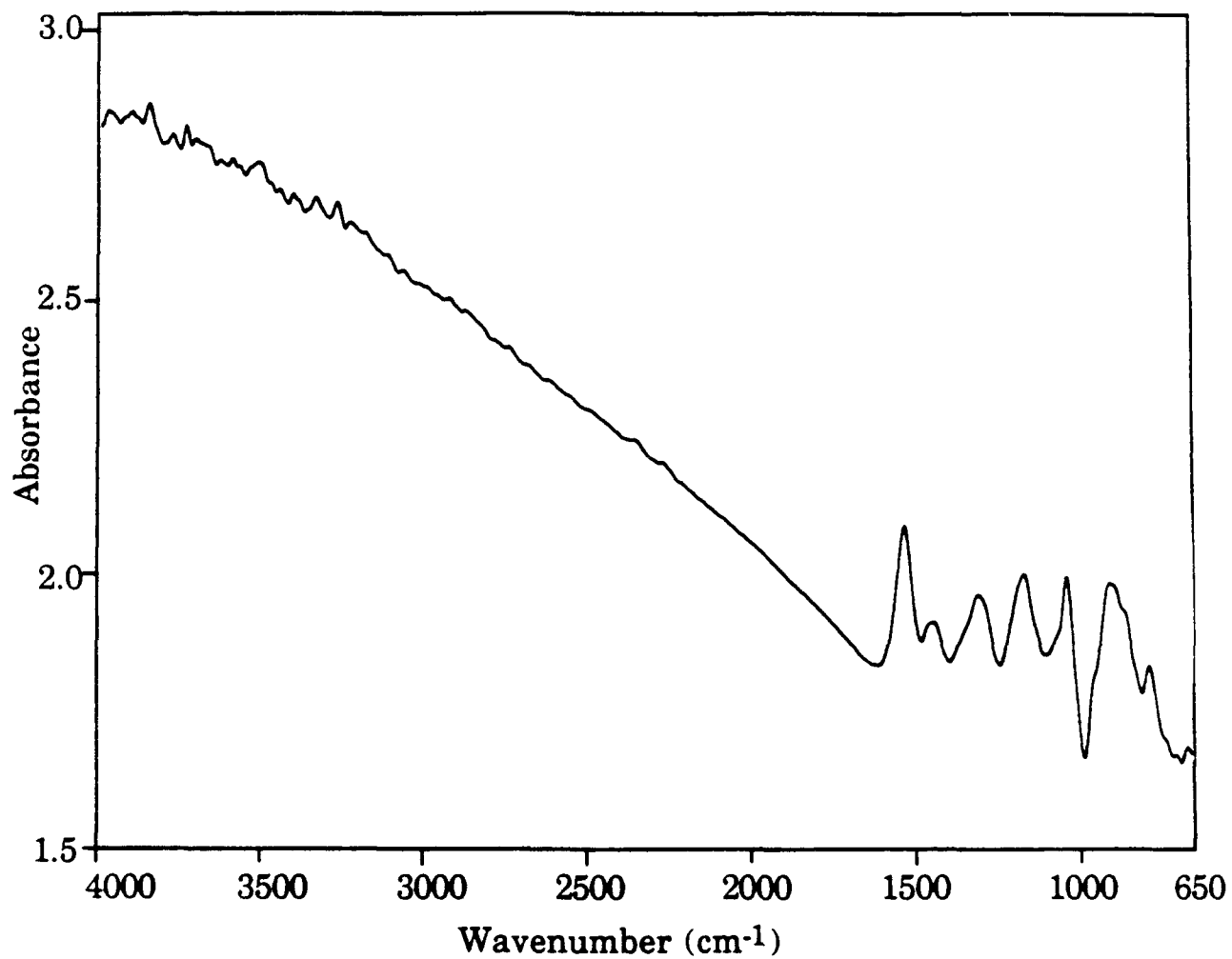


Fig. 1

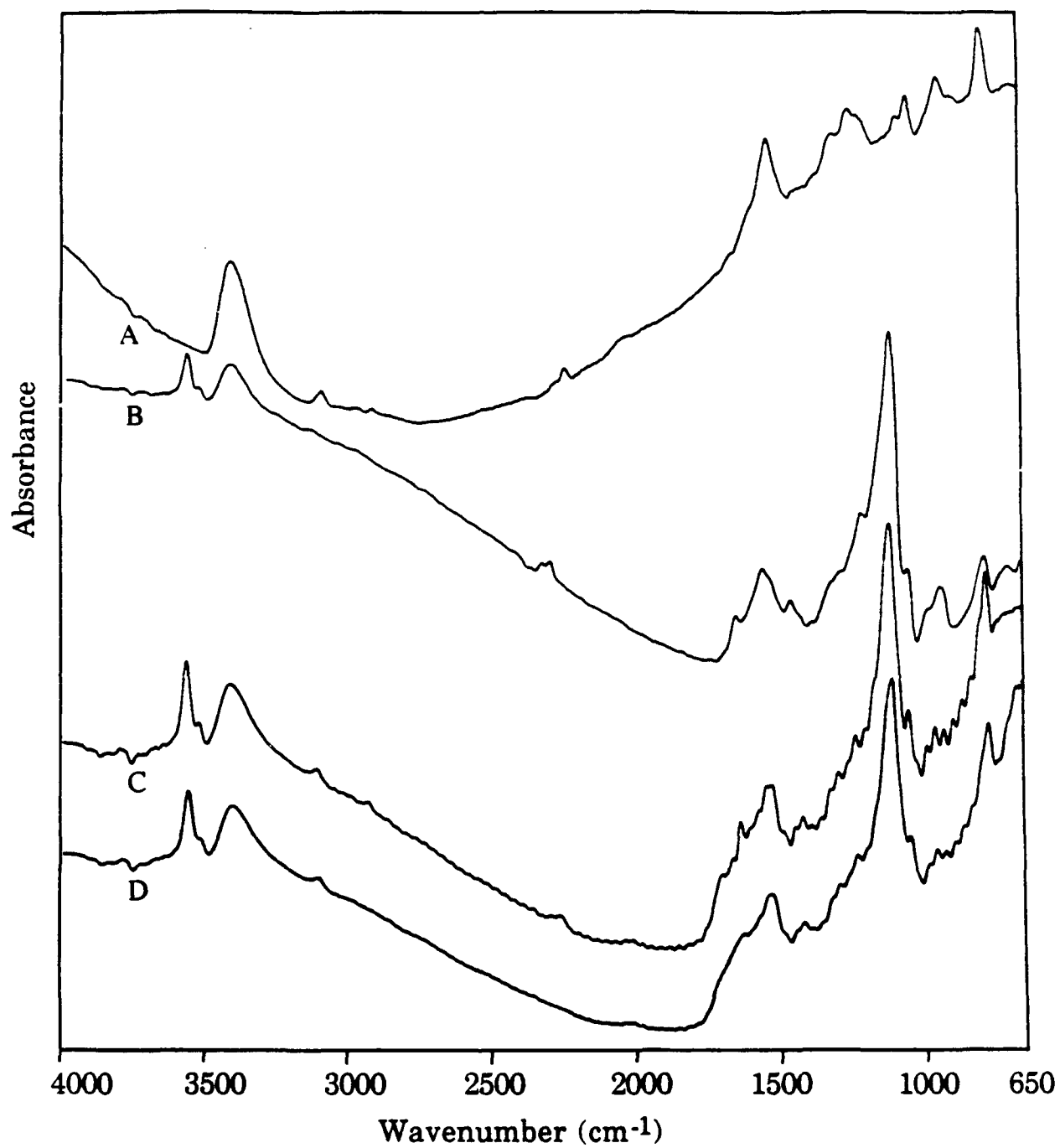


Fig. 2

